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Study of Plasma-Induced Surface Active Oxygen on Zeolite-Supported Silver Nanoparticles

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Abstract Surface oxygen induced by non-thermal plasma at atmospheric pressure on silver nanoparticle-loaded zeolite was determined by a chemical probe based on the oxidation of NO. The amount of active oxygen fixed onto the catalyst surface by O_2 plasma was approximately proportional to the square of the amount of supported silver. In dry air, its extraordinary long lifetime was confirmed for the first time.

Keywords Plasma-driven catalysis · Active oxygen · Silver nanoparticle · Atmospheric pressure

1 Introduction

Environmental issues and especially atmospheric pollution are of great concern throughout the world. Atmospheric-pressure non-thermal plasma (NTP) offers unique chemical environment that promotes the removal of air pollutants at low concentrations. On the other hand, the results of studies over the last 30 years have revealed several limitations of plasma-alone processes for practical use in industry. These include large energy consumption, low selectivity, and formation of unwanted byproducts. Plasma-catalyst hybrid technique is a promising technique to overcome these problems.

Combinations of atmospheric pressure dielectric barrier discharge (DBD) with different types of catalyst are currently being studied to improve the process performance [1–3]. These combinations have been experimentally proved to provide better selectivity for plasma and lower working temperature for catalyst [4–6]. For example, it has been reported that the combination of DBD and manganese catalyst enhances TCE decomposition and CO_2 selectivity [7, 8]. The loading of active metals not only enhances CO_2 selectivity for various VOCs [9–11], but also extends plasma area over the surface on catalyst [12].

The mechanism of synergistic effect, however, is still barely understood. Roland et al. [13] experimentally studied the stabilization of plasma-formed oxidants on the surface of $LaCoO_3$. When CO/N_2 mixture was fed to the O_2 plasma pretreated $LaCoO_3$ catalyst, the temporal profiles of outlet CO concentration changed according to the O_2 plasma pretreatment time. They concluded that the active oxygen formed by plasma treatment on the catalyst surface react with CO to produce CO_2 and thus improves the CO_2 selectivity, and that the active oxygen is the predominant active species for pollutant oxidation. The same group reported that oxygen atoms in the gas phase are available inside the nano-scale pores of γ-Al_2O_3 and silica gel, and porosity and specific surface of catalysts are therefore important for efficient pollutant decomposition [1]. Guaitella et al. [14] have shown that the plasma-pretreated TiO_2 in O_2 or air can remove C_2H_2 even in the absence of plasma and UV activation. They predicted that weakly bonded oxygen atoms may remain on TiO_2 long after plasma exposure and these react with C_2H_2. The adsorbed oxygen species were considered to play a key role in those experiments. More recently, our group reported isotopic evidence on NTP-induced fixation of gas-phase oxygen on the surface of several catalysts such as TiO_2, Ag/TiO_2, Ag/γ-Al_2O_3 and Ag/MS-13X at atmospheric pressure [15]. On-line mass spectrometric analysis and stoichiometric comparison of reactants and products revealed that the fixed

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surface oxygen can be activated by NTP, and it survived for a certain period of time (about 30 min).

The object of this letter is to investigate the effect of silver nanoparticles supported on zeolite for plasma-induced active oxygen on the catalyst surface. For this purpose, we quantitatively analyzed, by NO titration, the active oxygen species that was fixed by non-thermal O_2 plasma at atmospheric pressure onto the surface of zeolite-supported silver nanoparticles.

2 Experimental

The pellet-type zeolite (MS-13X, Sigma-Aldirch Co.) was used in this work. It had a diameter of about 1.6 mm, length of about 2.0–3.0 mm, and specific surface of 475 m^2/g. Silver nanoparticles were supported on the zeolite surface, at loadings of 5, 10, and 15 wt%, by an impregnation method using $AgNO_3$ as a precursor. After several drying processes, the catalysts were calcined at 500 °C in air for 10 h. Figure 1a, b show a TEM image of zeolite with 15 wt% of silver and diameter distribution of supported silver, respectively. The forms of supported silver nanoparticles were identified as hemispheres ca. 1–3 nm in diameter.

Figure 2 shows surface dielectric barrier discharge reactor and experimental setup. 1.5 g of catalyst was set in the effective region of plasma generated by a surface dielectric barrier discharge. The catalyst was held by silicon cap on either side. A stainless steel wire coil was set in contact with the inner wall of a quartz tube (o.d. = 12.5 mm, i.d. = 10.4 mm) as a barrier, and silver paste was painted on the outer side of the tube as the ground electrode. The effective length was 30 mm. A high-voltage amplifier (Model 20/20B, Trek Japan K.K., Japan) was used to apply high-voltage ac (100 Hz, 28 kV_{pp}) between the electrodes. The discharge power was 45 J/L as calculated by the V-Q method. Applied high-voltage was measured with a 1000:1 high-voltage probe (P6015A, Tektronix Corp., USA). The signals of voltage V and charge Q were recorded with a digital oscilloscope (Tektronix, TDS3034B Corp., USA). The area of V-Q parallelogram was calculated using an automated V-Q Lissajous program (V-Q Lissajous Program ver. 1.71, Insight Inc. Corp., Japan). The gas flow rate was fixed at 1.0 L/min using mass flow controllers (KOFLOC, FCC-3000). All experiments were conducted under dry conditions. Concentration of water vapor was less than about 80 ppmv, as measured by a dew point hygrometer (General Eastern, Hygro-M4 Model).

The active oxygen fixed by O_2 plasma pretreatment on catalyst surface was measured with NO oxidation method. The experimental procedure consists of several steps. First the catalysts were pretreated for 20 min under the conditions listed in Table 1. Then N_2 gas was supplied to remove all the gas phase species generated by plasma in the reactor. Afterwards the mixture of 100 ppm NO in N_2 was introduced and the outlet NO concentration was monitored by an on-line FT-IR spectrometer (Perkin-Elmer, Spectrum One) at 15 s intervals. The examples of FT-IR spectra were shown in Fig. 3. The experiment was repeated 30 times for each condition and the average values were plotted in Fig. 4. The gas temperature in reactor during plasma pretreatment was about 48° measured by fiber optic

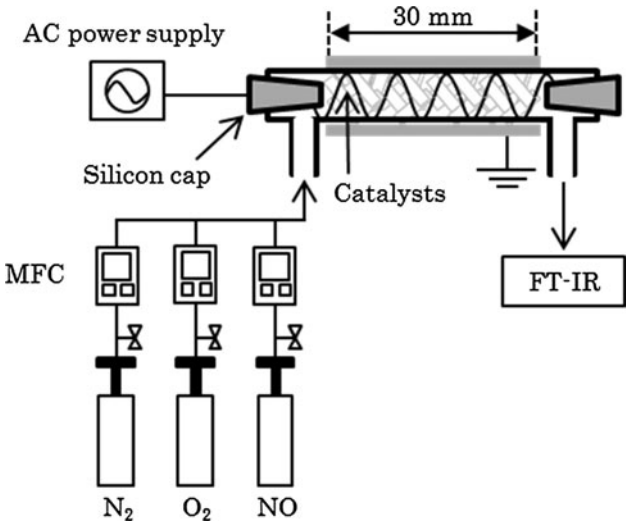

Fig. 2 Experimental setup

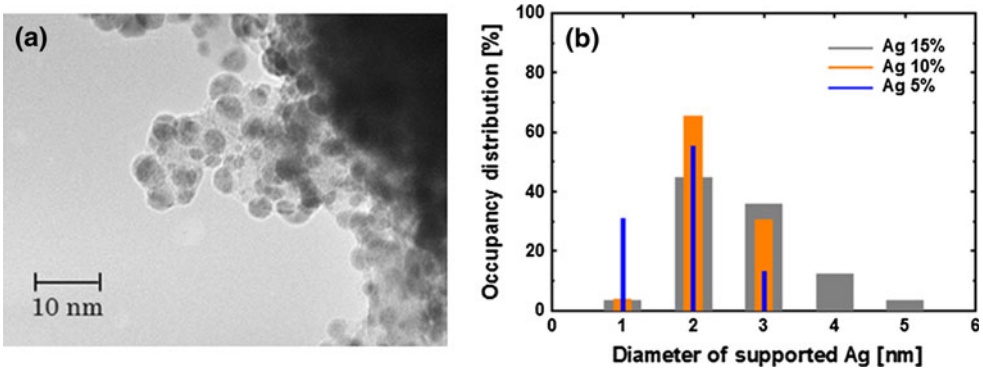

Fig. 1 **a** TEM image of Ag 15.0 wt%/MS-13X, **b** diameter distribution of supported silver nanoparticles

Table 1 Pretreatment condition

Condition	Ag amount on MS-13X	Plasma	Gas
a	No catalyst	×	O_2
b	15 wt%	×	O_2
c	0 wt%	○	O_2
d	5 wt%	○	O_2
e	10 wt%	○	O_2
f	15 wt%	○	O_2
g	15 wt%	○	N_2

○ and × show with and without plasma treatment, respectively

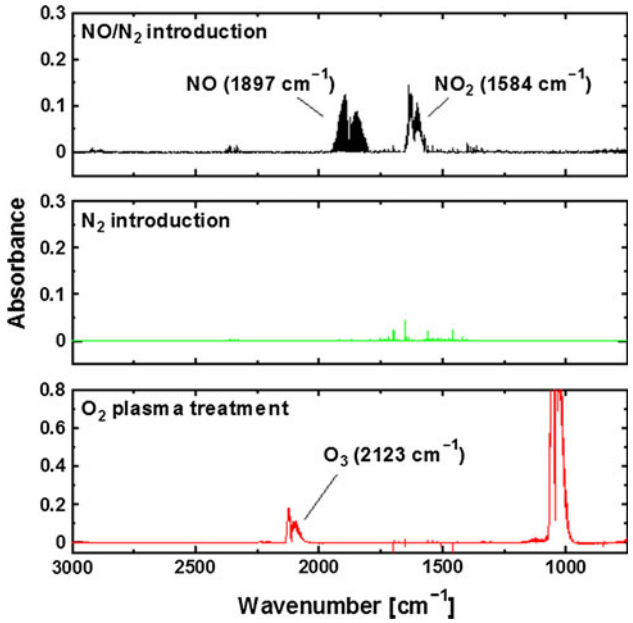

Fig. 3 FT-IR spectra

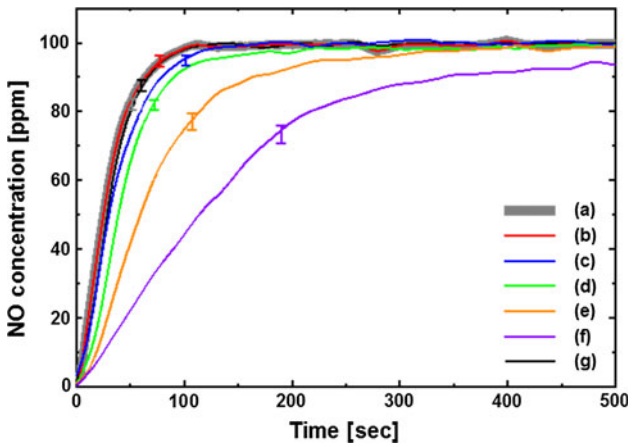

Fig. 4 Temporal profiles of NO concentration with catalysts pretreated under conditions described in Table 1

thermometer (AMOTH FL-2000, ANRITSU), and it was stable between start and end.

3 Results and Discussions

Figure 4 shows temporal profiles of outlet NO concentrations after the introduction of NO (100 ppm)/N_2. The letters (a–g) assigned to the curves in Fig. 4 correspond to the conditions described in Table 1. Adsorption of NO on the tested catalysts was found to be negligible, since the temporal profiles were identical regardless of whether catalyst was present, as can be seen in (a) and (b) in Fig. 4. This observation validates the NO titration method for measuring the plasma-induced surface oxygen. The small shift in the rise time induced by O_2 plasma pretreatment for silver-unloaded zeolite (compare (a) and (c) in Fig. 4), could be due to NO oxidation reaction with fixed active oxygen on zeolite surface or with O_3 retained by zeolite. In either case, these were predicted to be low amount from the small shift.

On the other hand, noticeable changes of profiles (d, e, f) were observed with the silver-loaded zeolite pretreated by O_2 plasma. The surface active oxygen fixed by O_2 plasma pretreatment increased with increasing amount of supported silver and it is assumed that the concentration of NO decreased by its oxidation reaction with active oxygen on the catalyst surface. In other words, the Ag nanoparticles played the key role in the fixation of oxygen species, which in turn led to the enhanced reactivity. However, there was a possibility that plasma created (i) new adsorption sites or (ii) active sites such as lattice defects on catalyst surface. To find out the influence of these two factors on NO reduction, the N_2 plasma pretreatment was applied to silver-loaded zeolite. In this case, a decrease in NO concentration was not observed (Fig. 4g). It indicates that plasma pretreatment is unable to create new adsorption sites and active sites on catalyst surface; thus, influence on NO reduction by (i) and (ii) can be ruled out in this experiment. Moreover, rapid rise of NO_2 concentration was detected at the time of NO introduction for silver-loaded zeolite pretreated by O_2 plasma. This allows us to conclude that some active oxygen fixed by O_2 plasma pretreatment oxidizes NO to NO_2. Such oxidizing ability was also confirmed by CO titration and CO_2 detection (data not shown).

Although the amount of active oxygen fixed by plasma on catalysts can be estimated indirectly from the amount of NO_2 emission, this method is subject to large errors due to a high adsorption capability of zeolite for NO_2. Therefore, the amount of active oxygen was estimated from the amount of removed NO which is integrated value of the differences of NO concentration between (a) and (c–f) in Fig. 4. For all the different loadings of silver, the amount

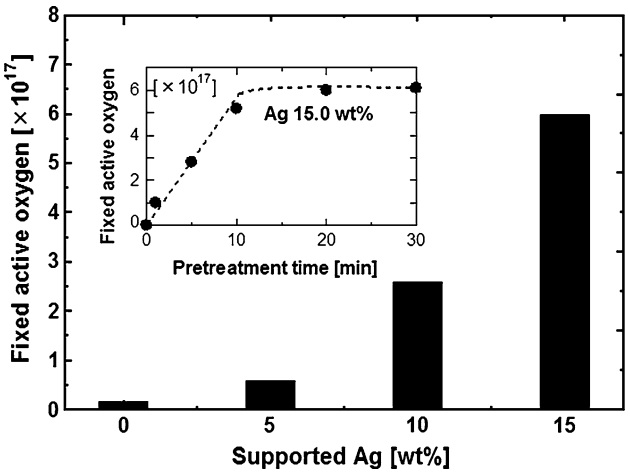

Fig. 5 Amount of plasma-induced surface oxygen species as a function of the amount of supported silver. *Inset* shows amount of fixed active oxygen as a function of pretreatment time

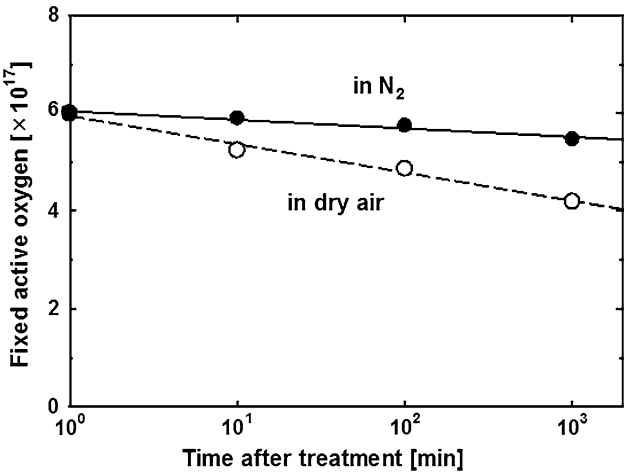

Fig. 6 Lifetime of plasma-induced surface oxygen species in N_2 and in dry air

of fixed active oxygen was proportional to the pretreatment time up to 10 min and then leveled off (an example is shown in inset of Fig. 5). Furthermore, the final amounts of fixed active oxygen, which are shown in Fig. 5, were proportional to the square of the amounts of supported silver. This effect can be explained by extension of plasma area over the catalyst surface with the increasing amount of supported silver nanoparticles.

The surface density of active oxygen on silver nanoparticles was roughly calculated from the data in Figs. 1 and 5. Based on the assumption that supported silver particles were hemispherical with diameter of 2 nm, the total surface area of silver at the loading of 15 wt% was estimated to be 60.1 m^2, and the surface density of active oxygen on catalyst was calculated to be 1.0×10^{12} cm^{-2}. Roland et al. [13] have reported that the surface density of active oxygen fixed by O_2 plasma pretreatment on $LaCoO_3$ was estimated to be about $1–2.5 \times 10^{12}$ cm^{-2} using CO oxidation reaction. The comparison of the surface density of active oxygen between $LaCoO_3$ and zeolite-supported silver nanoparticles indicates that both materials have similar capabilities of oxygen storage during O_2 plasma.

The decay of fixed active oxygen was studied in different gas environments using the catalyst pretreated under the condition denoted as (f) in Table 1. Following plasma pretreatment, N_2 or dry air was supplied during 1, 10, 100, and 1000 min. Afterwards the residual active oxygen on catalyst was determined by same method as previously described.

The lifetimes of surface-fixed oxygen in N_2 or dry air are shown on the Fig. 6. More than 90 and 70 % of initial amount of active oxygen survived for 1000 min in N_2 and dry air atmosphere, respectively. By contrast, in dry air the gas phase highly reactive oxygen species, atomic oxygen, electron-excited oxygen etc., decreased to 10 % or less by the three-body reaction within 100 μs after the discharge [16]. Such short lifetimes are one of the factors in performance limitations of the plasma-alone processes. The interaction of plasma with catalyst can fix gas-phase reactive oxygen on the surface of silver-loaded zeolite, and significantly extend the lifetime of fixed active oxygen.

4 Summary

In the present study, plasma-induced surface active oxygen on silver nanoparticles-loaded zeolite has been investigated at atmospheric-pressure using NO titration. The amount of active oxygen fixed by O_2 plasma on catalyst surface was approximately proportional to the square of the amount of supported silver, and it was proportional to pretreatment time up to 10 min and then leveled off. Additionally, in N_2 and dry air extraordinary long lifetime of fixed active oxygen was confirmed for the first time. These results indicate that supported silver nanoparticles on zeolite play significant role for performance improvement in plasma-catalyst hybrid technique, and proposed an explanation for the synergy in plasma-catalyst hybrid process.

In future work, identification of plasma-induced surface active oxygen species are required for detailed understanding of reaction mechanisms on plasma-catalyst hybrid process.

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